NOTE ON THE OCCURRENCE OF STRYCHNICINE.

By James M. Petrie, D.Sc., F.I.C., Linnean Macleay Fellow of the Society in Biochemistry.

(From the Physiological Laboratory of the University of Sydney.)

Strychnos psilosperma is a small tree, endemic in northern New South Wales, and Queensland. Its leaves possess a bitter taste, and are found to contain the little-known alkaloid strychnicine, accompanying strychnine and brucine.

Occurrence.—Strychnicine was discovered by Dr. van Boorsma, in 1902.* He isolated this alkaloid from the leaves of *Strychnos nux-vomica*, detecting it even in their earliest stages. He also found it in the pulp of the ripe fruit, in the hard shell, and in the thin orange-coloured skin of the fruit. The seeds contained a trace, and sometimes none. It was also identified in the leaves of *Strychnos tieuté* of Java; and was shown to be absent from the bark and wood of both these species. In the former it is associated, in the leaves, with both strychnine and brucine, while in the latter species with strychnine only.

Van Boorsma likewise tested *Strychnos laurina* and *S. monosperma* (E. Indies), leaves and branches, both young and old, but found no strychnicine.

Since its discovery, in 1902, this alkaloid has apparently been entirely neglected. The original paper, occurring in a botanical journal, published in the Dutch East Indies, has probably not been available to all workers; and perhaps for this reason, the *Strychnos* species which have been examined, other than those mentioned, have not been tested for strychnicine.

Separation of Strychnicine.—The leaves of *Strychnos psilosperma* were extracted with alcohol, the solvent distilled off *in*

* Bull. de l'instit. bot. de Buitenzorg, xiv., 1902, 3.

vacuo, and the residue dissolved in acidulated water. From this solution, containing alkaloids, the colouring matter was removed with ether and chloroform; then, on adding a slight excess of sodium hydroxide, the alkaloids were precipitated, and extracted with chloroform. The extract was shaken with acidulated water, and back into chloroform, a number of times in succession. Finally, the chloroform was distilled off, and the residue converted into sulphates, which were then dissolved in hot water and crystallised. The alkaloids readily separated in this way, and left in the mother-liquor a small amount of brucine, and most of the glucoside loganin, which imparted to the solution its characteristic purple tint.

The sulphates of the combined alkaloids were recrystallised from water and alcohol, and this left a peculiar green fluid, which gradually changed to brown on long standing. This point was observed also by Hooper* in his examination of *S. nux-vomica* leaves, and stated by him to be due to an acid resin.

The white crystallised sulphates were next dissolved in the minimum quantity of water, and precipitated by a considerable excess of sodium hydroxide. Van Boorsma states that the strychnicine redissolves under these conditions. The precipitate which was separated by the centrifuge, consisted of strychnine, and the supernatant fluid was examined for strychnicine. On the addition of more alkali to this fluid, further deposition took place of a bulky precipitate, first white, then turning to pink, brown, and dark brown. This precipitate appeared also to be easily soluble on adding a very little water, and was removed by shaking out with chloroform. The remaining aqueous solution, and from which nothing more could be removed by chloroform, still gave a Mayer reaction when tested, and became fluorescent when acidulated; it, however, did not taste bitter. The chloroform-extract then contained that portion of the alkaloids which was not permanently precipitated by sodium hydroxide. After removal of the chloroform, and dissolving in dilute sulphuric acid, to the solution, potas-

* Pharm. Journ. xxi., 1890, 493.

sium ferrocyanide was added, in order to separate any strychnine. This ferrocyanide precipitate and filtrate were separately examined.

Results.—The small ferrocyanide precipitate, when extracted with ammonia and chloroform, and the latter distilled off, left a residue, which—(1) gave all the general reactions for alkaloids, (2) with sulphuric acid and bichromate did not give the characteristic colour-reaction for strychnine, (3) gave no red colouration with nitric acid. This ferrocyanide precipitate, therefore, contained an alkaloid, which was not strychnine, and not brucine.

The filtrate from the ferrocyanide was also shaken out with alkali-chloroform, the solvent removed by distillation and the residue tested: (1) It gave all the general alkaloidal reactions, (2) it did not give the strychnine colour-test with sulphuric acid and bichromate, but (3) gave a faint positive reaction with nitric acid for brucine. The ferrocyanide filtrate, therefore, also contained an alkaloid, which was not strychnine, and in which only a trace of brucine was detected.

The alkaloid in both ferrocyanide precipitate and filtrate, when dissolved in a little dilute acid, gave precipitations with Wagner and Mayer solutions, picric, phosphotungstic, phosphomolybdic, tannic acids. When treated with excess of sodium hydroxide and filtered, the solution gave with hydrochloric acid the purple colour due to strychnicine, a reaction which the discoverer states to be characteristic of this new alkaloid. Barium hydroxide in excess and the solution then acidified with hydrochloric acid, also gives the characteristic purple reaction.

References.—It is noteworthy that, in the literature on the Strychnos species, before van Boorsma's discovery, there are definite indications of a probable new alkaloid; for example, Shenstone (Journ. Chem. Soc. 37, 1880, 235) states, that the igasurine of Desnoix is a mixture of strychnine and brucine, with a trace of some persistent impurity. Koefoed (Chem. Zeit., Mar. 16, 1889, 78; thro. Pharm. Journ. xix., 864) shows evidence which led him to conclude, that commercial strychnine and brucine each contain two

alkaloids. Fractional crystallisation of the platinum salts gave two different compounds containing different amounts of Pt.; the molecular difference represented CH_2, and the author distinguished the new compound by the prefix "homo." Hooper (Pharm. Journ. xxi., 1890, 493) in his investigation of the constituents of the leaves of *S. nux-vomica,* found that potassium ferrocyanide gave only a small precipitate, but that this did not possess the properties of strychnine; it did not give the sulphuric-bichromate reaction.

Summary.—The alkaloid discovered by van Boorsma in 1902, in the leaves of *Strychnos nux-vomica,* and named by him, strychnicine, is identified in the leaves of the Australian endemic species, *Strychnos psilosperma.* This strychnicine is found in the mother-liquor, after separating strychnine and brucine by sodium hydroxide and crystallisation. It is only partially precipitated by ferrocyanide, on long standing at a low temperature. It is recognised by its giving all the general alkaloid reactions, by giving a negative result for strychnine with sulphuric and bichromate, and a negative brucine result with nitric acid. Its solubility in sodium hydroxide, and its colour-reaction with barium or sodium hydroxide and hydrochloric acid are characteristic.

I am indebted to Mr. F. Turner, F.L.S., for the supply of material, which was sent to him by Dr. Bancroft, from North Queensland, and to both I take this opportunity of expressing my thanks. I have also to thank Professor Anderson Stuart for laboratory accommodation and facilities.